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COMPLETE SPECIFICATION

Hydroxyalkyl Amylose

GT. BRIT. 140
DIV. 170

We, A.E. STALEY MANUFACTURING CO., a corporation organized under the laws of the State of Delaware, United States of America, of Decatur, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with hydroxyalkyl amylose and with the hydroxyalkylation of amylose suspensions with vicinal epoxy compounds.

The expression "hydroxyalkyl amylose" as used in connection with the present invention includes the reaction products of amylose or chemically modified amylose with vicinal epoxy compounds.

It is well known that starch can be fractionated into two major fractions called amylose and amylopectin. Amylose is the straight chain portion of starch while amylopectin is the branched chain portion of starch. Various techniques have been developed to fractionate starch and this invention is directed to the amylose fraction of starch.

It is known that on cooling, aqueous pastes of unmodified starch above about 3.5% solids concentration set up and form a rigid gel or lose the ability to flow freely. At about the same time the phenomenon called "retrogradation" takes place. This involves the formation of a water-insoluble solid material, which will not redisperse in water. This property of gelling is very pronounced in pure amylose solutions. Even 1% pastes or solutions of amylose will gel and deposit practically the whole solute in the form of crystalline sediment in the course of a few days.

Specification No. 895,429 discloses broadly the concept of etherifying aqueous solutions of amylose, where the amylose has been dissolved in water by boiling under pressure or else heated in the presence of a peptizing agent. The only specific example of the preparation of an amylose ether in this specification is

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the reaction of amylose with dimethyl sulphate in a highly alkaline aqueous medium, which pastes the amylose. The amylose ether is then isolated by evaporating off the water on hot rolls. 50

Specifically, the present invention provides a readily isolable hydroxyalkyl amylose as hereinbefore defined having a molar substitution of at least 0.15, which is substantially water-insoluble at temperatures up to 100°C. and which forms at temperatures in excess of 100°C. an aqueous solution which neither gels nor retrogrades on subsequent cooling to room temperature. 60

The present invention also provides a film-forming, cold water-soluble, non-gelling hydroxyethyl amylose product assaying on an average at least 0.15 mole of ethylene oxide per anhydroglucose unit of amylose. 65

The present invention also provides a flexible hydroxyalkyl amylose film assaying on an average at least 0.15 mole of an alkylene oxide per anhydroglucose unit of amylose. 70

The present invention also provides a flexible hydroxyalkyl amylose film assaying on an average in excess of 0.15 mole of propylene oxide per anhydroglucose unit of amylose. 75

The present invention also provides a method of preparing hydroxyalkyl amylose as hereinbefore defined which comprises the steps of reacting at a temperature of from 30°C to 90°C. a suspension of amylose with at least 0.20 mole of a *vic*-epoxy compound and at least 0.04 mole of an alkaline catalyst per mole of amylose, wherein the suspending liquid is a polar solvent for the *vic*-epoxy compound, neutralizing the suspension, and isolating cold water-insoluble hydroxyalkyl amylose. 80

The present invention also provides a method of preparing hydroxyalkyl amylose film which comprises the steps of reacting at a temperature of from 30°C. to 90°C. a suspension of amylose with at least 0.20 mole of a *vic*-epoxy compound and at least 0.04 mole of an alkaline catalyst per mole of amylose, wherein the suspending liquid is a polar 85 90

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solvent for the *vic*-epoxy compound, neutralizing said alkaline suspension, partitioning the insoluble hydroxyalkyl amylose from the suspending liquid, dispersing the partitioned hydroxyalkyl amylose in water, heating the hydroxyalkyl amylose dispersion to a temperature above 100°C. until the hydroxyalkyl amylose goes into solution, distributing the hydroxyalkyl amylose solution as a thin layer on a surface and then forming a self-supporting film by evaporating the liquid.

Although hydroxyalkyl starches and the hydroxyalkylation of starch suspensions are both well known, no hydroxyalkyl starches are known which form continuous films having either good flexibility or high tensile strength. Further, the hydroxyalkylation of starch in aqueous alkaline suspensions has been limited to reaction mixtures wherein less than 0.2 mole of alkylene oxide per mole of starch is present, since the starch loses its granular form when more than 0.2 mole of alkylene oxide per mole of starch is reacted with starch. One object of this invention is to prepare a non-retrograding, non-gelling, cold water-soluble hydroxylalkyl amylose, which forms continuous films having good flexibility and high tensile strength, by reaction of a suspension of amylose with an alkylene oxide. A further object is to prepare a hydroxyalkyl amylose, which not only can be isolated without the use of costly techniques, such as spray drying or precipitation, but also can be readily put into aqueous solution in starch cooking equipment, said hydroxyalkyl amylose solution having little or no tendency to retrograde or to gel on cooling to room temperature.

In one aspect, this invention is a film, made from initially cold water-insoluble hydroxyethyl amylose which has subsequently been rendered soluble in cold water. The hydroxyalkyl amylose has a molar substitution between 0.15 and 0.39.

In a second aspect, this invention is a hydroxyalkyl amylose film, which is water-soluble at room temperature, having a molar substitution of at least about 0.40.

In a third aspect, this invention is a film-forming, cold water-soluble hydroxyalkyl amylose, which has little or no tendency to gel or retrograde when dissolved in water at room temperature.

In a fourth aspect, this invention is an initially cold water-insoluble, hydroxyalkyl amylose, which can be rendered water-soluble at temperatures in excess of 100°C, and when so solubilized has little or no tendency to gel or retrograde on cooling to room temperature. The hydroxyalkyl amylose solution may be spray dried forming a cold water-soluble hydroxyalkyl amylose powder or it can be cast directly to prepare hydroxyalkyl amylose films.

In a fifth aspect, the invention is a method of reacting an alkylene oxide with an alkaline

suspension of amylose in order to form an initially cold water-insoluble hydroxyalkyl amylose.

In another aspect, the invention is a method of preparing a film-forming, cold water-soluble hydroxyalkyl amylose powder. This product is prepared by dissolving initially cold water-insoluble hydroxyalkyl amylose in water at temperatures in excess of 100°C. and then isolating a cold water-soluble product either by precipitation with organic materials or evaporation of the water on hot rolls or by spray drying.

In still another aspect, the invention is a method of forming films from cold water-soluble hydroxyalkyl amylose by dissolving in water and then casting as films.

In somewhat greater detail, the hydroxyalkyl amylose of this invention is prepared by bringing a *vic*-epoxy-compound into contact with amylose in suspension in the presence of an alkaline catalyst. The reaction mixture is heated at a temperature of from 30°C to 90°C for preferably approximately 1 to 24 hours, and the catalyst is then neutralized. The resulting hydroxyalkyl amylose is then isolated.

The hydroxyalkyl amylose, which is substantially water-insoluble at this point, may be partitioned from the suspension medium by filtering or centrifuging and washing with water. This step may be characterized as the "solvent change" partitioning step. After washing, the water-insoluble hydroxyalkyl amylose particles may be dissolved in water by suspending the water-insoluble hydroxyalkyl amylose in water and then heating to between 100°C and 200°C. The hydroxyalkyl amylose, which is now water-soluble, can be partitioned from water-insolubles by filtering or centrifuging. The hydroxyalkyl amylose can then be recovered from the aqueous solution as a cold water-soluble product or as a film. The specific steps and modifications of this process will become clearer as the description proceeds.

REACTANTS

The amylose used in the aforementioned suspension may be in a crystalline form, a spray-dried form, or in an amorphous form. The crystalline form can be prepared by any technique, such as those discussed in Kerr, Chemistry and Industry of Starch, Second Edition, 1950. The spray-dried form, which may be partly crystalline and partly amorphous, is prepared by heating the crystalline form in the presence of water to approximately 150°C in an autoclave and spray-drying the resulting amylose solution. A substantially amorphous amylose is prepared by precipitating the amylose from aqueous solution with acetone. The crystalline amylose, spray-dried amylose and amorphous amylose may be prepared from the amylose fraction of any starch or modified starch. It is immaterial, for the purpose of this invention, whether the amylose

fraction is from corn starch, potato starch, wheat starch, rice starch, tapioca starch, sago starch. The modified starches include for example hypo-chloride-oxidized starch, enzyme treated starch, and acid-treated starch.

5 The alkylene oxides used in this invention may be characterized as vicinal epoxy compounds wherein the epoxy group is attached to adjacent carbon atoms. Included among
10 these compounds are ethylene oxide, 1,2-propylene oxide, 1,2-butylene oxide, and 2,3-butylene oxide. At least 0.20 mole of alkylene oxide per mole of amylose must be present in the reaction vessel in order to get a hydroxy-
15 alkyl amylose having a molar substitution of at least 0.15. While the molar ratio of alkylene oxide to amylose may be as high as 8:1 or higher, we have found that when low concentrations of catalyst are used, the highest molar
20 substitution occurs when from two to four moles of alkylene oxide are used for each mole of amylose. The catalyst concentration, duration of the reaction, temperature of the reaction, the presence of oxygen in the reaction
25 vessel, and the specific alkylene oxide all affect the reaction of alkylene oxide with amylose. Simple experiments may be run to determine, for particular conditions, the mole ratio of alkylene oxide to amylose necessary. The
30 numerous examples set forth in this specification illustrate the wide range of effective operating conditions.

The alkaline catalyst for this reaction may be any solvent-soluble alkaline material. The
35 catalyst may be an alkali metal hydroxide, such as sodium hydroxide or potassium hydroxide; an alkaline earth hydroxide, such as calcium hydroxide or barium hydroxide; a tetraalkyl ammonium hydroxide, such as tetramethyl
40 ammonium hydroxide; a tetraalkyl phosphonium hydroxide, such as tetraethyl phosphonium hydroxide; pyridine; an alkali metal alcoholate, such as sodium alcoholate or potassium alcoholate. For each mole of amylose
45 reacted, at least .04 mole of alkaline catalyst is necessary. When the catalyst concentration drops below .04 mole per mole of amylose, the resultant hydroxyalkyl amylose, after dissolving in water at elevated temperatures, has
50 a tendency to gel on cooling to room temperature. While a catalyst concentration as low as .04 mole per mole of amylose may be employed, it is preferable to use approximately .08 mole of catalyst per mole of amylose in
55 order to get the best results. When the catalyst concentration is less than .08 mole per mole of amylose, oxygen has a decided effect on the reaction. Under the conditions of the alkylation reaction, the oxygen present in the reaction
60 vessel appears to oxidize the amylose. Such oxidation of amylose discolors the amylose to an extent dependent on the amount of oxygen present. More important, the carboxyl groups of the oxidized amylose appear to neutralize
65 the catalyst with the attendant curtailment of

the reaction. When the reaction fails to go to completion, the hydroxyalkyl amylose formed does not have the desired properties and its aqueous solutions tend to gel when at room temperature. On the other hand, when .08 mole
70 catalyst per mole of amylose is used, the reaction can tolerate the presence of dissolved oxygen in the solvent as well as varying amounts of oxygen from the atmosphere without significant curtailment of the reaction.
75 However, it is usually preferable to keep the oxygen concentration within the reaction vessel at a minimum in view of the aforementioned possibility of discoloration.

Catalyst concentrations above .08 mole per
80 mole of amylose may be used. However, it is preferable to use as low a catalyst concentration as possible in order to reduce the amount of water-soluble or water-insoluble salts formed when the catalyst is neutralized. The
85 presence of excess salts in the hydroxyalkyl amylose film reduces the tensile strength of the film. Although the concentration of salts may be reduced by partitioning, which is discussed in detail below, it is economically desirable
90 to avoid such additional steps. With relatively pure amylose, a low concentration of catalyst permits avoiding both partitioning steps; when crude amylose is used, the first partitioning
95 step can be avoided. This cuts down the cost of the product without sacrificing its quality.

Any mineral acid or organic acid may be used to neutralize the catalyst. It is usually preferable to use strong acids, such as hydrochloric acid, sulfuric acid, benzenesulfonic acid
100 and phosphoric acid. However, acetic acid has been quite effective. While most of these acids form water-soluble salts when neutralizing the aforementioned alkaline catalysts, sulfuric acid neutralizes barium hydroxide forming a highly
105 water-insoluble salt. When crude amylose is hydroxyalkylated using barium hydroxide as the catalyst and sulfuric acid as the neutralizing acid, the concentration of the catalyst may be considerably above .08 mole per mole of
110 catalyst, since crude amylose contains other water-insolubles, which should be removed by partitioning the water-soluble hydroxyalkyl amylose, as discussed in detail below. On the other hand when an organic polar solvent is
115 used as the suspending liquid, the catalyst and neutralizing acid used should be selected in order to form a water-soluble salt on neutralization, since the water-soluble salt will be removed in the solvent change partitioning step.
120 Sodium hydroxide and hydrochloric acid have been used together very effectively. The concentration of the alkaline catalyst is accordingly not critical where an organic polar solvent is used. Concentrations as high as .8
125 mole of alkaline catalyst per mole of amylose have been used quite effectively.

The suspension medium for the reaction can be any polar solvent in which the epoxy compound is soluble. The preferred polar solvents
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are water; alcohols, particularly lower alkyl alcohols of 1 to 6 carbon atoms such as methanol, ethanol, 2-propanol, or butanol; and ethers, such as dioxane. Of these, water is most preferable because of economic considerations. We have also found that when an organic solvent is used to suspend the amylose, a small quantity of water acts as a catalyst, and increases the molar substitution of the hydroxyalkyl amylose.

PROCESS

More specifically, the hydroxyalkyl amylose of this invention is prepared by adding the epoxy compound to an alkaline suspension of amylose. In view of the gaseous state and high vapor pressure at room temperature of some alkylene oxides, such as ethylene oxide (B.P. 11°C), the alkylene oxide is either bubbled through the suspension or else liquefied before it is added to the reaction vessel. The reaction mixture may be cooled below the boiling point of the alkylene oxide, if desired. Although it is preferable, because of the low boiling point of some alkylene oxides, to add the alkaline catalyst and amylose to the suspension medium prior to the addition of the alkylene oxide, the catalyst and/or amylose may be added to the suspension medium after the alkylene oxide is added. This reaction may be run in an open vessel or in a closed vessel. When an open vessel is used, allowance must be made for any loss of alkylene oxide from the reaction vessel.

The hydroxyalkylation reaction is preferably carried out for from about 1 to 24 hours at between 30°C and 80°C. At temperatures between 0°C and 30°C, the reaction is quite slow and requires a relatively large quantity of catalyst. At temperatures between 80°C and 90°C, the hydroxyalkyl amylose is noticeably swollen and hard to filter. Above 90°C, the hydroxyalkyl amylose is so swollen that partitioning is virtually impossible.

When a polar organic solvent is used to suspend the amylose, the reaction mixture, which has been maintained at a temperature of from 30°C to 90°C for approximately 1 to 24 hours, is neutralized with an acid to a pH of between 6 and 8. At this point the hydroxyalkyl amylose is substantially insoluble in water. The product is separated by filtration or centrifuging and then washed with water. As previously stated, this step is the "solvent change" partitioning step. During the washing, essentially all water-soluble impurities in the amylose and water-soluble salts formed by the neutralization of the catalyst are removed. This product can be sold without further treatment to the manufacturer of films, who carries out the remaining steps in the process. The washed, water-insoluble, hydroxyalkyl amylose is then dispersed in about 5 to 20 times its weight of water and rapidly heated to form 100°C to 150°C or higher. After a short

time (1 second to 15 minutes) at this temperature, the hydroxyalkyl amylose suspension is converted to a non-gelling aqueous solution of hydroxyalkyl amylose, and the solution is cooled to room temperature. The temperature required to solubilize the hydroxyalkyl amylose suspension decreases as the molar substitution of the hydroxyalkyl amylose increases. Any water-insoluble solid impurities in the starting amylose and water-insoluble salts formed during the neutralisation of the catalyst may be removed from the hydroxyalkyl amylose solution at this point by a second partitioning step, for example, by filtering or centrifuging the insolubles from the solution.

As is apparent from the foregoing, the two separation steps enable us to prepare relatively pure hydroxyalkyl amylose from impure amylose without difficulty. Likewise, these two separation steps permit the use of large quantities of catalyst without any salt contamination of hydroxyalkyl amylose. Water-insoluble solid impurities in the amylose fraction used to make the hydroxyalkyl amylose of this invention and water-insoluble salts from the neutralized catalyst are readily removed from the aqueous hydroxyalkyl amylose solution by partitioning. Likewise, any water-soluble impurities in the amylose and any water-soluble salts from the neutralized catalyst are easily removed in the solvent-change partitioning step, immediately following the neutralization step.

While the procedure set forth in the preceding paragraphs may be followed when water is used as the polar suspending liquor, it is preferable, when carrying out the whole process in one plant, to simplify this procedure by omitting the solvent change partitioning step. This step can be omitted, since even relatively crude amylose has a low concentration of water-soluble impurities. Furthermore, at the conclusion of the reaction, the hydroxyalkyl amylose is dispersed in water, and this dispersion is immediately useful in the next step. Accordingly, the neutralized aqueous suspension of hydroxyalkyl amylose is rapidly heated in an autoclave to a temperature of from about 100°C to 150°C or higher until a non-gelling, hydroxyalkyl amylose solution is formed as described before. Any water-insoluble solid impurities may be removed from the hydroxyalkyl amylose solution by partitioning at this point, as by filtration or centrifugation.

It is evident from the preceding paragraph that the aqueous hydroxyalkylation system is dependent upon the selection of catalyst concentrations and/or the combination of catalyst and neutralizing acid, which will permit the omission of the solvent-change partitioning step. As stated previously, in the discussions of the catalyst and neutralizing acid, the solvent change partitioning step can be advantageously omitted when the catalyst concentration is low (approximately 0.04 mole catalyst per mole

of amylose up to 0.16 mole of catalyst per mole of amylose) or when the catalyst and neutralizing acid are selected in such a way that they form a water-insoluble salt.

5 Whether water or a polar organic solvent has been used, and whether the aqueous solution produced by the high-temperature treatment is filtered or not, a cold water-soluble hydroxyalkyl amylose powder is recovered
10 from the solution by precipitation with an organic material, such as acetone, or by evaporating the water on hot rolls or by spray drying. Instead of isolating the hydroxyalkyl amylose as a powder, it may be cast directly
15 into a film.

The hydroxyalkyl amylose products of this invention are classified in four distinct types which are: initially water-insoluble products, which can be rendered water-soluble at temperatures in excess of 100°C; cold water-soluble hydroxyalkyl amyloses; cold water-soluble hydroxyalkyl amylose films. The initially water-insoluble hydroxyalkyl amyloses can be separated from the hydroxyalkylation reaction
20 medium in the solvent-change partitioning step. The initially water-insoluble hydroxyalkyl amylose can be used to prepare cold water-soluble hydroxyalkyl amyloses or hydroxyalkyl amylose films.

30 The cold water-soluble hydroxyalkyl amylose powders are prepared by dissolving initially water-insoluble hydroxyalkyl amyloses in water at temperatures in excess of 100°C, followed by either precipitating the hydroxyalkyl amylose powder from solution with an organic material or by evaporating the water on hot rolls or by spray drying. The cold water-soluble hydroxyalkyl amylose whose aqueous solutions are non-gelling has a molar substitution of at least 0.15, i.e., on an average 0.15
35 mole of alkylene oxide on each anhydroglucose unit of amylose. When the molar substitution is below 0.15, an aqueous solution of hydroxyalkyl amylose, which has been prepared by dissolving cold water-soluble hydroxyalkyl amylose in water, tends to form a gel at room temperature. Likewise, initially water-insoluble hydroxyalkyl amylose having a molar substitution below 0.15, which has been dissolved
40 in water at elevated temperatures, tends to gel on cooling to room temperature. It is, accordingly, not practical to cast films from hydroxyalkyl amylose, which has a molar substitution below 0.15, since its solutions tend to gel rapidly at room temperature.
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50 The preferred cold water-soluble hydroxyalkyl amyloses of this invention have a molar substitution in excess of 0.19. At room temperature aqueous solutions of hydroxyalkyl amyloses, which have a molar substitution of about 0.15 to about 0.19, do have some tendency to gel or retrograde at concentrations of from about 10% to 20% by weight hydroxyalkyl amylose; on the other hand, aqueous
55 solutions of hydroxyalkyl amylose, which have

a molar substitution in excess of 0.19 do not gel or retrograde at these concentrations. However, the hydroxyalkyl amyloses, which have gelled or retrograded at the above concentrations readily dissolve in hot water.

70 The cold water-soluble, hydroxyalkyl amyloses of this invention, having a molar substitution of 0.15 and above, are excellent film formers and have little or no tendency to gel or to retrograde in aqueous solutions. Two classes of films are formed. The first class, which has a molar substitution of about 0.40 and above, is water-soluble at room temperature. These films can be used to package bleach, soap, starch or other materials where
75 it is desirable to dissolve the film packaging in water.

The second class of films, whose molar substitution ranges from 0.15—0.39, are water-insoluble at room temperature but soluble in boiling water. It is believed the retrogradation occurs during drying of these films. This insolubilization of the cast film is particularly surprising since the solutions from which the films are cast have virtually no tendency to gel or to retrograde. The films themselves are self-supporting and flexible with high tensile strength and are useful in many types of packaging.
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85 The following examples are merely illustrative and should not be construed as limiting the scope of the invention.

EXAMPLE 1.

69.7 grams of amylose (64.8 grams on a dry solids basis or .4 mole) was slurried in 500 ml. of water. 83 ml. of water was used to transfer the slurry to a 32 oz. beverage bottle. After cooling to between 5—8°C, 1.30 grams NaOH (1.80 ml. of a 50% solution) was added to the slurry. Allowing 1 gram for loss, 18.7 grams (approximately 0.4 mole) of ethylene oxide (at 5—8°C) was poured into the weighed bottle from a graduated cylinder. Part of the ethylene oxide, which boils at around 11°C, flushed the lighter air out of the bottle and caused ice to form in the bottle before the bottle was capped with a butyl rubber-lined cap. The bottle was reweighed and tumbled for 16 hours in a water bath, which was maintained at 50°C. The suspension was then cooled to room temperature and neutralized with 5N HCl to a pH of 7. A small portion of the sample was precipitated in excess acetone, and vacuum-oven dried. The remainder of the slurry was shaken to effect complete suspension, and about 10 ml. of the suspension was quickly poured through a long-stemmed funnel into a 15 × 20 × 250 mm. Pyrex Carius combustion tube. The tube was sealed and then heated for five minutes in a 150°C oil bath, and the suspension was thereby converted to a clear viscous solution. It was noted that the solution did not gel and there was no evidence of retrogradation after the tube had been cooled to room temperature. This sample was
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subsequently poured into an aluminum foil dish. The water-insoluble film which formed on drying could be bent through 180° without breaking.

- 5 The balance of the slurry was placed in a three-liter jet cooker. The structure and operation of the jet cooker are discussed in detail in Specification No. 895,215. The slurry was jet cooked for 15 seconds at 150°C and
10 then cooled to room temperature at which it was a stable, clear, viscous solution. This solution was spray dried forming a white cold water-soluble powder. A small sample, which was analyzed by treatment with hydriodic
15 acid, indicated that the hydroxyethyl amylose had a molar substitution of 0.38.

EXAMPLE 2.

- 20 A series of samples in seven-ounce beverage bottles was prepared in order to illustrate the effect of various ratios of ethylene oxide to amylose. Approximately 0.05 mole of amylose

(8.46 grams, 7.86 grams on a dry solids basis) was slurried in 50 ml. water. Thirty mls. of water was used to transfer each slurry to a seven-ounce bottle. The bottles were cooled
25 to between 5 and 8°C. and 0.16 gram of NaOH (4 ml. of 1 N solution) was added. The pH of all the samples was between 11 and 12. Allowing 1 gram for loss, the various mole quantities of ethylene oxide (at 5—8°C)
30 set forth in Table I were poured into each bottle. The bottles were capped with a butyl rubber-lined cap and tumbled end-over-end for 16 hours in a 50°C. water bath. Each slurry was cooled to room temperature and then
35 neutralized to a pH of 7 with about 4 ml. 1 N HCl. Prior to neutralization sample 8 had a pH of 10.6 while the other samples had a pH of about 8. Ten ml. samples of each slurry were solubilized in a Carius tube in the manner
40 described in Example 1 and then cooled to room temperature. The results are indicated in Table I.

TABLE I

Run	Moles Ethylene Oxide Per Mole Amylose	Molar Substitution	Appearance of Neutral, Undiluted Hydroxyethyl Amylose Solution After Standing for Two Weeks at Room Temperature
1	.125	.12	White, rigid gel
2	.25	.16	Soft gel
3	.5	.27	Clear liquid
4	1.0	.38	Clear viscous liquid
5	2.0	.76	Clear viscous liquid
6	4.0	.72	Clear viscous liquid
7	8.0	.19	Clear thin liquid
8*	8.0	.57	Clear viscous liquid

* In this run the bottle was purged with nitrogen prior to the addition of ethylene oxide.

- 45 Flexible films, which could be bent through an angle of 180° without breaking, were cast from solutions 4 to 7. The films prepared from the solutions of runs 5 and 6 were soluble in

water at room temperature. The films prepared from the solutions of runs 4 and 7 would
50 not dissolve in water at room temperature, but did dissolve in boiling after 5 minutes.

EXAMPLE 3.

5 This example illustrates the effect of varying both the catalyst-to-amylose and the alkylene oxide-to-amylose mole ratios on the gelling of hydroxyalkyl amylose solutions. Runs 5 and 10 show the additional effect of an inert atmosphere on the gelling of hydroxyalkyl amylose solutions.

Fifteen samples of amylose (8.46 grams, 7.86 grams on dry basis) were reacted at 50°C for 16 hours by the method set forth in Example 2, varying the concentration of the catalyst and of the ethylene oxide as set forth in Table II below.

10

TABLE II

Run	Moles Ethylene Oxide Per Mole Amylose	Moles NaOH Per Mole Amylose	Appearance of Neutral, Undiluted Hydroxyethyl Amylose Solution After one Month at Room Temperature
1	.125	.08	White, rigid gel
2	.125	.16	White, rigid gel
3	.25	.08	Soft gel
4	.25	.16	Clear, viscous liquid
5*	.5	.04	Clear, viscous liquid
6	.5	.08	Clear, viscous liquid
7	.5	.16	Clear, viscous liquid
8	1.0	.02	White, rigid gel
9	1.0	.04	White, rigid gel
10*	1.0	.04	Clear, viscous liquid
11	1.0	.08	Clear, viscous liquid
12	2.0	.02	White, rigid gel
13	2.0	.04	White, rigid gel
14	2.0	.08	Clear, viscous liquid
15	4.0	.02	White, rigid gel
16	4.0	.04	White, rigid gel
17	4.0	.08	Clear, viscous liquid

* In these runs the bottles were purged with nitrogen prior to the addition of ethylene oxide. Flexible films were cast from solutions 4, 5, 6, 7, 10, 11, 14, and 17.

EXAMPLE 4.

This example illustrates the effect of temperature on the hydroxyalkylation. Seven samples of amylose (8.46 grams, 7.86 grams on a dry solids basis) were reacted at a tem-

perature of from 30°C—90°C for 16 hours by the method set forth in Example 2 using 3.2 grams ethylene oxide (approximately .05 mole) and 0.16 gram NaOH. The results are set forth in Table III.

TABLE III

Run	Temperature	Appearance of Neutral, Undiluted Hydroxyethyl Amylose Solution After One Month at Room Temperature
1	30° C.	Clear, viscous liquid
2	40° C.	Clear, viscous liquid
3	50° C.	Clear, viscous liquid
4	60° C.	Clear, viscous liquid
5	70° C.	Clear, viscous liquid
6	80° C.	Clear, thin liquid
7	90° C.	Clear, thin, amber liquid

EXAMPLE 5.

This example illustrates the use of propylene oxide as the alkylene oxide. A slurry of approximately .05 mole amylose (8.46 grams, 7.86 grams on a dry solids basis) in a seven-ounce beverage bottle was prepared by the method of Example 2. After adding 0.16 gram NaOH, N₂ was bubbled through the suspension to remove all oxygen from the bottle. After addition of 2.64 grams of 1,2-propylene oxide (5—8°C) to the cold bottle (5—8°C), it was capped with a butyl rubber-lined cap and tumbled end-over-end for 16 hours in a water bath maintained at 50°C. The bottle was cooled to room temperature and neutralized with approximately 4 ml. of 1 N HCl. A 10 ml. sample of the suspension was solubilized in a Carius tube by the method described in Example 1. The cooled solution was clear and viscous. A clear, flexible, water-insoluble film was prepared by pouring the solution into an aluminium foil dish and drying. Another sample of the suspension was filtered, washed in acetone and analyzed. The product had a molar substitution of 0.28.

EXAMPLE 6.

Example 5 was repeated using 3.08 grams commercial 1,2-butylene oxide instead of propylene oxide. The cooled Carius tube solution was clear. The product had a molar substitution of 0.29.

Various substituted alkylene oxides can be reacted in the same manner such as styrene oxide, 9,10 epoxystearic acid, 3-(diethylamino) 1,2-epoxy propane, epoxidized soybean acids. These compounds are representative of alkylene oxides substituted with aryl groups, carboxyl groups and amino groups.

EXAMPLE 7.

This example illustrates the use of potassium hydroxide as the alkaline catalyst.

Example 2, run #4, was repeated using as a catalyst 0.23 gram KOH instead of 0.16 gram NaOH. The cooled Carius tube solution was clear and viscous. The product had a molar substitution of 0.38 as did the product of Example 2, run #4.

EXAMPLE 8.

This example illustrates the catalytic effect of potassium hydroxide, sodium hydroxide, sodium alkoxide and water where an organic solvent is employed as the suspension medium. Seven hundred and twenty-four grams of acetone-wet amylose (200 grams amylose dry basis) was slurried with 500 ml. isopropyl alcohol, filtered, pressed to remove excess solvent and reslurried with 600 ml. isopropyl alcohol. The slurry was weighed and divided in eight equal portions, which were added to 12-ounce beverage bottles (25 grams amylose on dry solids basis in each bottle). After the addition of catalyst (see Table IV), each of the bottles was evacuated until the isopropyl alcohol boiled and then brought back to atmospheric pressure with N₂ gas. Nine grams ethylene oxide (5—8°C) was added to each bottle (5—8°C). The bottles were capped and then tumbled end-over-end in a 50°C water bath for the time indicated. The contents were neutralized with acetic acid and filtered. The separated solid was washed with acetone and dried in a vacuum oven. The products were water-insoluble, but after treatment in a jet cooker, as described in Example 2, and spray drying, they were cold water-soluble. The results are displayed in Table IV.

TABLE IV

Run	Catalyst Added	Moles Catalyst Per Mole Amylose	Time in Hours	Molar Substitution
1	1 gram sodium dissolved in 60 grams isopropyl alcohol	.28	4	.48
2	3 grams NaOH (4 ml. of 50% aqueous NaOH diluted with 5 ml. of additional water)	.49	4	1.1
3	2 grams KOH dissolved in 30 ml. isopropyl alcohol	.23	4	.36
4	2 grams KOH dissolved in 30 ml. isopropyl alcohol and 5 ml. water	.23	4	.69
5	1 gram Na dissolved in 60 grams isopropyl alcohol	.28	20	1.2
6	3 grams NaOH (4 ml. of 50% aqueous NaOH diluted with 5 ml. of additional water)	.49	20	.84
7	2 grams KOH in 30 ml. isopropyl alcohol	.23	20	1.0
8	2 grams KOH in 30 ml. isopropyl alcohol and 5 ml. water	.23	20	1.1

EXAMPLE 9.

- 5 This example illustrates the results obtained with a relatively high ratio of alkaline catalyst to amylose. 10
- Three samples of amylose (8.46 grams, 7.86 grams on a dry solids basis) were reacted at 50°C for 16 hours using 2.6 ml. of 50% NaOH (approximately 0.8 mole NaOH per mole of amylose), by the method set forth in Example 2. The results are set forth in Table V.

TABLE V

Run	Moles Ethylene Oxide Per Mole Amylose	Appearance of Neutral, Undiluted Hydroxyethyl Amylose Solution After One Month at Room Temperature
1	.25	Clear thin liquid
2	.50	Clear thin liquid
3	1.00	Clear thin liquid

EXAMPLE 10.

- 15 This example illustrates the results obtained with .05 mole of alkaline catalyst per mol of amylose at 70°C.
- 20 An aqueous slurry of approximately 0.04 mole amylose (48.7 grams aqueous slurry, 6.48 grams on a dry solids basis) in a seven-ounce beverage bottle was diluted with 44 ml. water. Two mls. 1 N NaOH (0.05 mole per mole of amylose) was added to the bottle. After cooling to between 5—8°C, 3.52 grams of ethylene oxide was added to the bottle. The capped bottle was tumbled end-over-end at 70°C for 16 hours, cooled, and then neutralized. The
- 25

sample was heated in a Carius tube as described in Example 1. The cooled Carius tube sample was a clear, viscous solution at room temperature.

5 EXAMPLE 11.

This example illustrates the preparation of non-gelling hydroxyalkyl amylose solutions where the hydroxyalkylation is completed in a relatively short time (1.5 or 2 hours).

10 Two samples of amylose (8.46 grams, 7.86 grams on a dry solids basis) were run at 50°C by the method set forth in Example 2 using 3.2 grams ethylene oxide and 0.16 gram NaOH. After
15 reacting for 1.5 hours one sample was neutralized. The second sample was neutralized after two hours. Each sample gave a clear, colorless solution after Carius tube heating. These solutions did not gel on standing two
20 weeks at room temperature.

EXAMPLE 12.

This example illustrates the use of an open vessel. One hundred and ten grams of amylose (100 grams on a dry solids basis or .62 mole)
25 was stirred into a 2 liter resin kettle containing 800 ml. of water. The resin kettle was equipped with a dry ice reflux condenser and a stirrer. After .1 mole of NaOH was added to the

kettle, the kettle was evacuated with an aspirator pump and the air was replaced with nitrogen. After 5.43 grams (.17 mole) of ethylene oxide was added to the kettle, it was placed in a water bath, which was maintained at 50°C for 16 hours. The reaction mixture was neutralized to pH 7 with about 21 ml. of 5
35 N HCl. The hydroxyalkyl amylose was filtered and then washed with water. The isolated hydroxyalkyl amylose had a molar substitution of .18. An aqueous solution of this product, which had been prepared by heating in a Carius tube one gram of product in 10 ml. water at 150°C, did not gel or retrograde on cooling to room temperature.

EXAMPLE 13.

Example 12 was repeated using 32.6 grams
45 ethylene oxide (.75 mole) instead of 5.43 grams ethylene oxide. The hydroxyalkyl amylose had a molar substitution of .70; the cooled Carius tube solution was clear.

EXAMPLE 14.

The following table illustrates the comparative physical properties of hydroxyethyl amylose films, a hydroxyethyl starch film and films formed from commercial cellulose products. All of these films were cast on glass from neutral
55 solutions.

TABLE VI

Film	Molar Substitution	Film Thickness in Mils	Tensile Strength in psi	% Elongation at Break
Hydroxyethyl Starch***	0.5	1.3	1000	too small to measure
Hydroxyethyl Amylose	0.38	2.1	4540	24
Hydroxyethyl Amylose	0.38	2.5	4830	18
Hydroxyethyl Amylose	0.38	2.9	4770	13
Hydroxyethyl Amylose	0.38	3.4	4720	12
Hydroxyethyl Amylose	0.43	4.0	4760	8
Hydroxyethyl Amylose	0.43	4.8	4480	10
Hydroxyethyl Amylose	0.43	5.8	4170	12
Hydroxyethyl Amylose	0.90	2.7	3490	23
Hydroxyethyl Amylose	0.90	3.2	3360	24
Hydroxyethyl Cellulose*	1.04	3.5	4000	37
Hydroxyethyl Cellulose**	1.61	2.9	2570	62
Hydroxyethyl Cellulose**	1.61	3.3	2690	66

* "Cellosize" WP-09 ("Cellosize" is a Registered Trade Mark).

**Natrosol.

*** The hydroxyethyl starch values were taken from Vol. 37, No. 5, page 667 of *Cereal Chemistry*, September, 1960.

As is well known, the analysis for oxyethylene units is not completely accurate. Accordingly, the numerical value of the molar substitutions recited in the specification and claims is to be interpreted as being within experimental error.

WHAT WE CLAIM IS:—

1. A readily isolable hydroxyalkyl amylose as hereinbefore defined having a molar substitution of at least 0.15, which is substantially water-insoluble at temperatures up to 100°C. and which forms at temperatures in excess of 100°C. an aqueous solution which neither gels nor retrogrades on subsequent cooling to room temperature.

2. The amylose of claim 1 which is a hydroxyethyl amylose.

3. A film-forming, cold water-soluble, non-gelling hydroxyethyl amylose product assaying on an average at least 0.15 mole of ethylene oxide per anhydroglucose unit of amylose.

4. A flexible hydroxyalkyl amylose film assaying on an average at least 0.15 mole of an alkylene oxide per anhydroglucose unit of amylose.

5. The film of claim 4 in which the alkylene oxide is ethylene oxide.

6. A flexible hydroxyalkyl amylose film assaying on an average in excess of 0.15 mole of propylene oxide per anhydroglucose unit of amylose.

7. A method of preparing hydroxyalkyl amylose as hereinbefore defined which comprises the steps of reacting at a temperature of from 30°C. to 90°C. a suspension of amylose with at least 0.20 mole of a *vic*-epoxy compound and at least 0.04 mole of an alkaline catalyst per mole of amylose, wherein the suspending liquid is a polar solvent for the *vic*-epoxy compound, neutralizing the suspension, and isolating cold water-insoluble hydroxyalkyl amylose.

8. The method of claim 7 wherein the suspension is an aqueous suspension, the neutralized suspension is heated to a temperature above 100°C. until the hydroxyalkyl amylose dissolves, and the hydroxyalkyl amylose is then recovered.

9. The method of claim 7 which further

comprises the steps of separating the cold water-insoluble hydroxyalkyl amylose from the suspending liquid, dispersing the hydroxyalkyl amylose in water, heating the hydroxyalkyl amylose dispersion to a temperature above 100°C. until the hydroxyalkyl amylose dissolves and then recovering a cold water-soluble hydroxyalkyl amylose.

10. A method of preparing hydroxyalkyl amylose film which comprises the steps of reacting at a temperature of from 30°C. to 90°C. a suspension of amylose with at least 0.20 mole of a *vic*-epoxy compound and at least 0.04 mole of an alkaline catalyst per mole of amylose, wherein the suspending liquid is a polar solvent for the *vic*-epoxy compound, neutralizing said alkaline suspension, partitioning the insoluble hydroxyalkyl amylose from the suspending liquid, dispersing the partitioned hydroxyalkyl amylose in water, heating the hydroxyalkyl amylose dispersion to a temperature above 100°C until the hydroxyalkyl amylose goes into solution, distributing the hydroxyalkyl amylose solution as a thin layer on a surface and then forming a self-supporting film by evaporating the liquid.

11. The method of any of claims 7, 9 or 10 wherein the suspending solvent for the *vic*-epoxy compound is water, an alcohol or an ether.

12. The method of any of claims 7 to 11 wherein the *vic*-epoxy compound is ethylene oxide.

13. The method of any of claims 7 to 11 wherein the *vic*-epoxy compound is propylene oxide.

14. A method of preparing hydroxyalkyl amylose substantially as herein described with particular reference to examples 1 to 13.

15. A method of preparing hydroxyalkyl amylose film substantially as herein described with particular reference to the examples 1 to 13.

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